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ABSTRACT

The major objective of this research program is to determine the operational characteristics key to efficient, low-cost, stable liquid-junction and solid-state solar cells based on sensitized nanoporous films (in collaboration with DOE's Office of Science Program). Toward this end, we are conducting experimental and theoretical studies to understand the unique physical and chemical factors governing cell performance. Current scientific issues addressed include the influence of film morphology, sensitizer, and electrolyte on the electron transport and recombination dynamics and on the light-harvesting, charge-injection, and charge-collection efficiencies. Recently, we investigated the relationship between (1) transport and recombination, (2) morphological factors of core-shell nanoparticle films and their PV properties, and (3) electron-electron interactions and their effect on the transport dynamics [1-3]. In this paper, we discuss the connection between transport and recombination and its effect on cell performance [1].

1. Objectives

The purpose of this study [1] is to examine the validity of the current model for recombination in dye-sensitized solar cells [4]. In the conventional dye-sensitized cell, recombination is generally accounted for in terms of the following mechanism [4,5]:

$$I_3^- \underset{K_1}{\rightleftharpoons} I_2 + I^- \tag{1}$$

$$I_2 + e^- \xrightarrow{k_2} I_2^{\bullet -} \tag{2}$$

$$2I_2^{\bullet} \rightleftharpoons I_3^- + I^- \tag{3}$$

Triiodide in solution is assumed to be in equilibrium with molecular iodine on the TiO_2 surface (reaction 1), which reacts with photoinjected electrons (reaction 2). In a proposed rate-determining step, the resulting iodine radical anion ($I_2^{\bullet -}$) reacts with a second radical anion (reaction 3). There is no experimental evidence that confirms reaction 3 is rate determining. As an alternative mechanism, we have investigated whether electron transport to molecular iodine (reaction 2) is rate limiting [1].

Understanding the fundamental phenomena governing cell performance is critical for underpinning the development of this new solar cell technology. Of programmatic importance is that sensitized nanoparticle solar cells represent the distinct technological promise for achieving mass-produced, ultra-low-cost solar panels with good efficiency.

2. Technical Approach

Photocurrent and photovoltage transient studies, together with modeling, were used to determine whether electron transport limits recombination in dye-sensitized nanoparticle TiO_2 solar cells under their normal operating conditions [1]. To vary the rate of transport, TiO_2 films were electrochemically doped with Li^+ to produce traps. Photocurrent transient studies were used to investigate whether Li^+ doping slows transport and induces trap formation. A causal link between electron diffusion and recombination was studied by photocurrent and photovoltage transient techniques. A kinetic model was developed to account for experimental results. The effect of Li^+ doping on cell performance was also studied.

3. Results and Accomplishments

Spectroelectrochemical and transient measurements established that when Li^+ is present in the electrolyte, Li^+ intercalates irreversibly into TiO_2 films at open circuit (ca. 0.7 V) under normal solar light intensities [1]. Photocurrent transients of doped TiO_2 films indicate that Li^+ doping decreases the electron diffusion coefficient in the nanoparticle network. The electron diffusion time t_C displays a power-law dependence on the short-circuit photocurrent density J_{SC}, as is commonly observed. With increased Li^+ doping, the slopes of the plots increase. The power-law dependence is generally attributed to trap filling involving an exponential distribution of localized states adjacent to the conduction band [6,7] and movement of the quasi-Fermi level in response to changes in light intensity. With higher light intensity, the residence time of electrons in traps in the vicinity of the quasi-Fermi level decreases, resulting in faster transport. This model predicts that $t_C \propto J_{SC}^{a-1}$, where $m_c = kT/a$, m_c is the width of the trap-state distribution [1,6,7], T is the temperature, and k is the Boltzmann constant. Thus, the observed large increase of the slopes (m_c increasing from 60-400 meV) with higher Li^+ doping levels is ascribed to the widening of the exponential conduction band-tail resulting from disorder induced by randomly placed Li^+ defects in TiO_2.

Figure 1 shows the dependence of the time constants for electron diffusion and recombination t_R on J_{SC} for sensitized cells with nondoped and doped films. With increased doping of TiO_2 films, both electron diffusion and recombination times increase proportionately, indicating a causal link and suggesting that transport limits recombination in fully functional dye-sensitized solar cells, contrary to the assumption that reaction 3 is rate limiting.

A transport-limited recombination mechanism accounts for a number of observations. Assuming that the rate-limiting step involves the diffusion of electrons to surface-adsorbed molecular iodine (reaction 2) produced in the

chemical decomposition of I_3^- (reaction 1), the rate of recombination R is given by the expression $R = K_1 k_2 N [I_3^-]/[I^-]$, where $[I_3^-]$ and $[I^-]$ are the concentrations of the redox couple and N is the electron density in the film. For reaction 2 to be rate limiting, k_2 must be proportional to the electron diffusion coefficient D, which is inversely proportional to the diffusion time t_C. The recombination lifetime t_R, defined by the pseudo-first-order kinetics equation $R = N/t_R$, can be written with the aid of the rate of recombination expression as $t_R = N/R \propto 1/k_2 \propto 1/D \propto t_C$. This expression describes the connection between the recombination lifetime and the electron diffusion time. It can be shown that the diffusion-limited recombination model preserves the nonlinear dependence of the recombination rate on electron density N [4] via the dependence of the diffusion time on N [6,7].
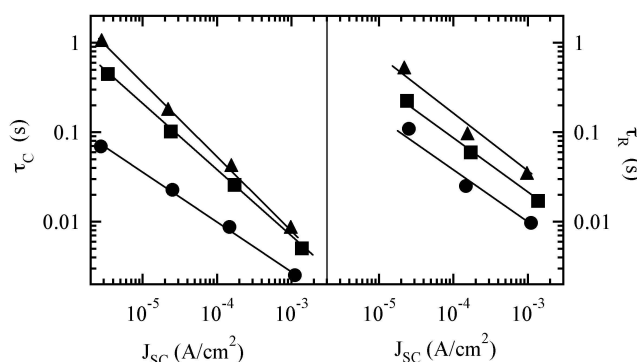

Fig. 1. Characteristic times for collection (τ_C – left panel) and recombination (τ_R – right panel) for dye-sensitized solar cells with nondoped (circles) and doped (squares and triangles) TiO$_2$ films. The triangles represent the most heavily doped film. The lines are power-law fits to the data.

The photovoltaic properties of the cell are largely unaffected by Li$^+$ doping because doping leaves the ratio t_C/t_R, and therefore the charge-collection efficiency [8], almost unchanged. The latter determines J_{SC}. The rate of recombination at one-sun light intensity is expected to change very little because the diffusion time, and accordingly, the rate constant k_2, displays only minor changes with doping at high light intensities (Fig. 1). Therefore, the open-circuit voltage of the cell [4] at one-sun light intensity is predicted to remain almost constant with doping. These predictions were verified experimentally [1].

4. Conclusions

The relationship between the loss mechanism and transport was investigated by photocurrent and photovoltage transient measurements and modeling. The results show that when TiO$_2$ films are electrochemically doped with Li$^+$, both electron diffusion and recombination times increase proportionately, indicating a causal link. The transient measurements along with kinetic analyses provide first evidence that electron diffusion limits recombination in the conventional dye-sensitized solar cells under their normal operating conditions and show that the rate of recombination is first order in iodine concentration.

Measurements also show that when Li$^+$ ions, which are commonly used in electrolytes for dye-sensitized solar cells, are present, they intercalate irreversibly into sensitized TiO$_2$ films under normal solar light intensities. Investigation of the dependence of the electron diffusion coefficient on the photoelectron density in the films at different Li$^+$ doping levels suggests that doping creates random defects causing disorder in the films, which widens the exponential conduction band-tail states. Although Li$^+$ doping is shown to occur during normal cell operation, its effect on the photovoltaic characteristics is found to be insignificant. These results suggest, contrary to conventional thought, that increasing the electron-transport rate will not significantly improve the solar cell performance.

Future work will investigate the effect of various electrolyte components and other factors (e.g., film morphology) on cell performance. Additional studies are planned to understand the transport mechanism, to gain further insight into possible approaches to improve cell efficiency. Also, the viability of quantum-scaled semiconductors as photosensitizers will be studied.

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